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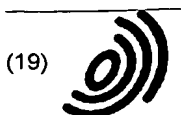
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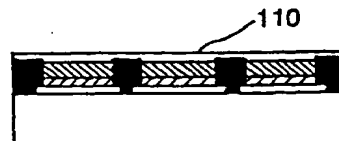
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(54) METHOD OF PRODUCING ORGANIC EL ELEMENT AND ORGANIC EL ELEMENT

(57) The composition for a hole injecting and transporting layer which pertains to the present invention is a composition for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, and comprises a conductive compound (the hole injecting and transporting layer component) and a solvent; the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of 30° to 170°, the viscosity is within the range of 1 cps to 20 cps, and the surface tension is within the range of 20 dyne/cm to 70 dyne/cm. Through these physical

characteristics, there is provided a composition for a hole injecting and transporting layer that allows optimization of material and element design to be carried out, and that allows high-precision patterning film formation to be carried out easily, in a short time, and at low cost.

Fig.1E



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## Description

[0001] The present invention relates to a manufacturing process for an organic EL (electroluminescence) element, an electrically light-emitting element that may be used in displays, display light sources, and the like. In particular, it relates to a composition for use as a hole injecting and transporting layer suitable for ink jet patterning.

## BACKGROUND ART

[0002] When electric charge is applied to a solid thin film containing a fluorescent organic molecule and sandwiched between electrodes, holes (holes) are injected from the anode and electrons from the cathode, these carriers moving through the thin film due to the applied electric field, and recombining. An element in which the energy released during this recombination is consumed in the formation of a singlet excitation state of the fluorescent molecule (molecule exciton), and the fluorescence emitted with relaxation of the singlet exciton to ground state is utilized is an organic EL element.

[0003] Apropos, with a single-layer type structure element comprising a light-emitting layer only, light emission efficiency is low and there are problems with durability, and therefore a two-layer type structure element provided with a hole injecting and transporting layer with good contact situated between the anode and the light-emitting layer has been proposed. Through the use of a stacked structure to control carrier injection/transport balance and carrier recombination location, EL light-emitting element light emission efficiency and durability can be improved. Further, according to a stacked structure, the functions of light emission and injection/transport can be carried out by separate materials, which provides the advantage of making possible optimal design of materials and elements.

[0004] In the past, as hole injecting and transporting layer compounds for two-layer stacked type organic EL elements, there have been proposed in the past a porphyrinic compound (US Patents 4,356,429 and 4,720,432), aniline, pyridine, and low-molecular weight derivatives thereof (Unexamined Patent Application (Kokai) 3-34382), hole injecting and transporting layers using carbon layers (Unexamined Patent Application (Kokai) 8-31573), etc. The formation of hole injecting and transporting layers using these low-molecular weight materials is usually accomplished by film formation methods involving vacuum deposition or sputtering. Polyaniline (Nature, 357, 477 (1992), etc. are known as low-molecular weight materials, film formation being carried out by a wet process such as spin coating, etc.

[0005] However, film formation methods involving vacuum deposition or sputtering are batch processes having extended time periods, and thus mass production efficiency is poor. In the case of low-molecular weight materials, there are the problems of susceptibility to crystallization after film formation and lower element reliability. On the other hand, in the case of high-molecular weight materials, there are the advantages of a high degree of freedom in molecular design, and ease of optimization of materials owing to a wet process; however, film formation methods such as spin coating, etc., have a big problem in that virtually all of the material is wasted.

[0006] In cases where fine patterning of materials is required, as in full-color displays, etc., there are the fundamental problems that high-precision patterning is difficult in deposition processes, while the materials lack durability against patterning processes involving photolithography. The same problems exist in the case of high-molecular weight materials as well. The materials used as hole injecting and transporting layers or buffer layers are conductive, and thus if complete patterning cannot be realized, this can result in leakage current between adjacent pixels located on a given substrate.

## DISCLOSURE OF THE INVENTION

[0007] Accordingly, it is an object of the present invention to provide a composition for hole injecting and transporting layers that allows optimization of material and element design to be carried out, and that allows high-precision patterning film formation to be carried out easily, in a short time, and at low cost. It is a further object to provide a manufacturing process for a composition for hole injecting and transporting layers. It is yet a further object to provide a manufacturing process for an organic EL element using this composition. It is yet a further object to provide an organic EL element manufactured by means of this manufacturing process and having excellent light emission characteristics.

[0008] The composition for a hole injecting and transporting layer which pertains to the present invention is a composition for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, contains a polar solvent for dispersing or dissolving a conductive compound for forming the hole injecting and transporting layer and a lubricant for facilitating ink-jet patterning, and has the following physical properties (contact angle, viscosity, surface tension).

## (1) Contact angle

[0009] In preferred practice, the contact angle of the composition for a hole injecting and transporting layer and the material making up the nozzle face of the ink-jet type recording head will be established within the range 30°-170°. Establishment within the range 35°-65° is especially preferred.

[0010] By means of the composition for a hole injecting and transporting layer having a contact angle of this range, bending of flight during discharge can be reduced, making possible precise discharge control. Where the

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contact angle is smaller than  $30^\circ$ , wetting of the composition for a hole injecting and transporting layer at the nozzle face increases, so that when the composition for a hole injecting and transporting layer is discharged, the composition for a hole injecting and transporting layer sometimes adheres asymmetrically about the perimeter of the nozzle hole. In this case, mutual attraction between the composition for a hole injecting and transporting layer adhering to the nozzle and the composition for a hole injecting and transporting layer which is being discharged acts in such a way that the composition for a hole injecting and transporting layer is discharged through uneven force, so that bending of flight occurs and the target location cannot be impacted. Further, the frequency of bending of flight increases. On the other hand, where the contact angle exceeds  $170^\circ$ , interaction between the composition for a hole injecting and transporting layer and the nozzle hole is at a minimum, and the shape of the meniscus at the nozzle distal end is not stable, with the result that the composition for a hole injecting and transporting layer discharge amount and discharge timing are difficult to control.

[0011] Bending of flight refers to misplacement of the impact location of the composition for a hole injecting and transporting layer by  $30\text{ }\mu\text{m}$  or more away from the target location when the composition for a hole injecting and transporting layer is discharged from the nozzle hole. Frequency of bending of flight refers to the time elapsed until bending of flight occurs during continuous discharge at an ink-jet type recording head piezoelectric thin film element oscillation frequency of 14.4 kHz, for example.

### (2) Viscosity

[0012] In preferred practice, the viscosity of the composition for a hole injecting and transporting layer will be in the range 1 cps-20 cps. Establishment within the range 2 cps-4 cps is especially preferred.

[0013] Where the viscosity of the composition for a hole injecting and transporting layer is below 1 cps, the meniscus of the composition for a hole injecting and transporting layer at the nozzle hole will not be stable, making discharge control difficult. On the other hand, where the viscosity exceeds 20 cps, it will not be possible to smoothly discharge the composition for a hole injecting and transporting layer from the nozzle hole, making ink discharge difficult unless the specifications of the ink-jet type recording head are modified, such as by making the nozzle hole bigger, etc. Where viscosity is high, the solid ingredients in the composition for a hole injecting and transporting layer will tend to precipitate, increasing the frequency of nozzle hole clogging.

### (3) Surface tension

[0014] In preferred practice, the surface tension of the composition for a hole injecting and transporting layer will be established in the range 20 dyne/cm-70 dyne/cm. Establishment within the range 25 dyne/cm-40 dyne/cm is especially preferred.

[0015] By establishing the surface tension within this range, bending of flight is reduced analogously to the contact angle described earlier, and the frequency of bending of flight can be reduced. Where surface tension is greater than 70 dyne/cm, the shape of the meniscus at the nozzle distal end is not stable, with the result that the composition for a hole injecting and transporting layer discharge amount and discharge timing are difficult to control. On the other hand, where surface tension is lower than 20 dyne/cm, wetting of the composition for a hole injecting and transporting layer with respect to the material of the nozzle face increases, so that, as with the contact angle described earlier, bending of flight occurs and the frequency of bending of flight becomes high.

[0016] This bending of flight occurs mainly when there is uneven wetting of the nozzle hole, when there is clogging due to adhesion of solid matter in the composition for a hole injecting and transporting layer, etc., and can be solved through cleaning of the ink-jet type recording head (hereinafter termed "flushing"). Flushing usually involves working the ink-jet type recording head mechanism so as to prevent clogging and bending of flight, the design being such that a prescribed amount of the composition for a hole injecting and transporting layer is forcedly discharged when discharge of the composition for a hole injecting and transporting layer has not been carried out for a given time (hereinafter termed "flushing time"). This flushing time refers to the time required for a nozzle to dry and give rise to bending of flight when not discharging the composition for a hole injecting and transporting layer, and is indicative of the properties of the composition for a hole injecting and transporting layer. The longer the flushing time, the more appropriate [the composition is] for ink-jet printing techniques, thus allowing the composition for a hole injecting and transporting layer to be discharged in a stable manner for extended periods.

[0017] Accordingly, by endowing the composition for a hole injecting and transporting layer with the physical properties mentioned earlier, it is possible to produce a longer flushing time and to maintain a more fresh state at the interface of the composition for a hole injecting and transporting layer with the air. It is additionally possible to produce uniform dot density of the composition for a hole injecting and transporting layer being discharged, thereby making it possible to prevent the occurrence of irregularities, etc., of the composition for a hole injecting and transporting layer. Further, since the linearity of flight is excellent, control of the ink-jet type recording head is facilitated, and a simple constitution may be adopted for the manufacturing equipment.

[0018] In preferred practice, a mixed solution of water and a lower alcohol (e.g., methanol, ethanol, etc.) will be used as the polar solvent. A mixed solution of water and a Cellosolve solvent (e.g., ethoxy ethanol, etc.) can also be used. In preferred practice, the lubricant will be glycerin. The manufacturing process for a composition for a hole injecting and transporting layer which pertains to the present invention may entail preparation via a sonication process and a filtration process.

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[0019] The manufacturing process for an organic EL element which pertains to the present invention is a manufacturing process for an organic EL element having a stacked structure of a hole injecting and transporting layer and a light-emitting layer formed within a partitioning member divided into individual pixel areas, comprising a step wherein a partitioning member provided with openings corresponding to pixel areas is formed on a substrate; a step wherein an ink-jet type recording head is used to fill the aforementioned openings with the composition for a hole injecting and transporting layer which pertains to the present invention; and a step wherein the composition for a hole injecting and transporting layer that has filled the openings is subjected to a drying process to form a hole injecting and transporting layer. Through this method, hole injecting and transporting layer film thickness, dot count, and other parameters may be controlled in a desired manner, allowing the size and pattern of the organic EL element to be established in a desired manner as well.

[0020] The organic EL element which pertains to the present invention is manufactured through the foregoing process, and the film thickness of the hole injecting and transporting layer is 0.1  $\mu\text{m}$  or less. The film resistance of the hole injecting and transporting layer is in the range  $0.5 \times 10^9 \Omega/\text{m}^2$  to  $5 \times 10^9 \Omega/\text{m}^2$ . By establishing the film thickness and the film resistance of the hole injecting and transporting layer within the preceding ranges, the light-emission characteristics of the organic EL element can be improved.

## BRIEF DESCRIPTION OF THE DRAWINGS

### [0021]

Fig. 1 is a sectional view of manufacturing steps for an organic EL element.

## BEST MODE FOR CARRYING OUT THE INVENTION

Embodiment of Invention 1.

[0022] A composition for a hole injecting and transporting layer, organic EL element manufacturing process, and organic EL element pertaining to an aspect of the present embodiment is described below.

[0023] The composition for a hole injecting and transporting layer principally contains a conductive compound for forming the hole injecting and transporting layer, a dispersant solvent, and a lubricant, and is used for pattern film formation through an ink-jet system. In preferred practice, the conductive compound for forming the hole injecting and transporting layer is a compound having lower ionization potential than the anode. For example, where ITO is used for the anode, examples of low-molecular weight materials would include copper phthalocyanine and other porphyrinic compounds.

[0024] Other additives, as well as film stabilizing materials, may be added as well; for example, viscosity modifiers, antioxidants, pH modifiers, preservatives, resin emulsions, leveling agents, etc., may be used.

(Example)

[0025] Using copper phthalocyanine as the conductive compound (hole injecting and transporting layer component), the physical characteristics of compositions for a hole injecting and transporting layer [produced therefrom] were studied. Composition 1 through Composition 10, given in Table 1 through Table 10, were prepared as specimens.

Table 1

| Composition 1                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | water   | 70            |
| Lubricant                                       | glycerin  | 5             |

Table 2

| Composition 2                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |

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| Composition 2 |            |               |
|---------------|------------|---------------|
|               | Ingredient | Content (wt%) |
| Polar solvent | water      | 65            |
|               | methanol   | 5             |
| Lubricant     | glycerin   | 5             |

Table 3

| Composition 3                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | water   | 65            |
|   | ethoxy ethanol  | 5             |
| Lubricant                                       | glycerin  | 5             |

Table 4

| Composition 4                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | methanol  | 70            |
| Lubricant                                       | glycerin  | 5             |

Table 5

| Composition 5                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | N, N-methyl formamide   | 70            |
| Lubricant                                       | glycerin  | 5             |

Table 6

| Composition 6                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | water   | 70            |
| Lubricant                                       | --  | 0             |

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Table 7

| Composition 7                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | water   | 70            |
|   | methanol  | 5             |
| Lubricant                                       | --  | 0             |

Table 8

| Composition 8                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | water   | 70            |
|   | ethoxy ethanol  | 5             |
| Lubricant                                       | --  | 0             |

Table 9

| Composition 9                                   |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | water   | 65            |
|   | butoxy ethanol  | 5             |
| Lubricant                                       | glycerin  | 5             |

Table 10

| Composition 10                                  |   |               |
|---|---|---------------|
|   | Ingredient  | Content (wt%) |
| Hole injecting and transporting layer Component | copper phthalocyanine (10 wt%) (styrene acrylic resin dispersion) | 25            |
| Polar solvent                                   | water   | 65            |
|   | isopropyl alcohol   | 5             |
| Lubricant                                       | glycerin  | 5             |

(Discharge Evaluation)

[0026] Composition 1 through Composition 8, given in Table 1 through Table 8, were measured for contact angle with respect to the nozzle face constituent material constituting the ink-jet type recording head, viscosity, and surface tension, and the discharge properties thereof were evaluated. The discharge evaluation was conducted using

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an ink-jet printing device (Epson MJ-500C).

[0027] Viscosity [is expressed as] measured values at 20°C. These results are given in Table 11.

Table 11

| Composition | Contact angle [°] | Viscosity [cps] | Surface tension [dyne/cm] | Discharge properties |
|-------------|-------------------|-----------------|---------------------------|----------------------|
| 1           | 135               | 3.8             | 62.8                      | O                    |
| 2           | 91                | 3.6             | 40.8                      | O                    |
| 3           | 62                | 3.1             | 39.8                      | Display Problem«     |
| 4           | 22                | 0.8             | 23.1                      | X                    |
| 5           | 175               | 0.9             | 81.0                      | X                    |
| 6           | 118               | 1.1             | 71.0                      | X                    |
| 7           | 28                | 0.8             | 68.8                      | X                    |
| 8           | 27                | 0.9             | 69.2                      | X                    |

[0028] From these results, it will be apparent that a contact angle of 30° to 170°, and especially 35° to 65°, is preferred. Further, viscosity of 1 cps to 20 cps, and especially 2 cps to 4 cps is preferred, and surface tension of 20 dyne/cm to 70 dyne/cm, and especially the range 25 dyne/cm to 40 dyne/cm, is preferred.

[0029] Composition 1 through Composition 3, which contain glycerin as a lubricant, when compared to Composition 6 through Composition 8, which do not contain a lubricant, may be seen to be superior in terms of discharge properties. Accordingly, in preferred practice, the ink composition will contain a lubricant. The inclusion of a lubricant can effectively prevent drying and solidification of the ink composition in the nozzle mouth. Examples of the lubricant are glycerin, diethylene glycol, and other polyhydric alcohols; glycerin is especially preferred.

(Manufacturing process for composition for a hole injecting and transporting layer)

[0030] Composition 1 through Composition 3, Composition 9, and Composition 10 given in Table 1 through Table 3, Table 9, and Table 10, respectively, were manufactured, and the particle size distribution of the hole injecting and transporting layer-forming compound (copper phthalocyanine) was measured before and after a sonication. Using the preceding compositions for a hole injecting and transporting layer having been passed through a filtration step subsequent to the sonication the film forming properties of hole injecting and transporting layers formed through ink-jet system patterning were evaluated.

[0031] These results are given in Table 12. Sonication results are expressed as the proportion of the particle size distribution of 1 µm or smaller.

[0032] Particle size in the styrene acrylic resin dispersion was 1 µm or above.

Table 12

| Composition | 1 µm particle size proportion (%) |                  | Film forming properties |
|-------------|-----------------------------------|------------------|-------------------------|
|             | before sonication                 | after sonication |                         |
| 1           | 4.8                               | 46.8             | O                       |
| 2           | 2.8                               | 31.4             | O                       |
| 3           | 4.2                               | 43.5             | Display Problem«        |
| 9           | 2.5                               | 18.5             | X                       |
| 10          | 3.9                               | 18.2             | X                       |

[0033] From the preceding results, it will be apparent that 4-hour sonication of the dispersion can increase dispersion. Further, by additionally filtering the sonicated dispersion, it is possible to achieve a more homogeneous hole injecting and transporting layer film. As the dispersant polar solvent for the conductive compound, water or a mixed solvent of water and methanol or ethoxy ethanol is preferred (Composition 1 through Composition 3); it will be apparent that, where these solvents are used, film forming properties are good.

(Organic EL element manufacturing steps)

[0034] Using Composition 1 through Composition 3 given in Table 1 through Table 3, patterning film formation of hole injecting and transporting layers by an ink-jet system was carried out by the following procedure to manufacture



organic EL elements.

Anode formation step (Fig. 1A)

[0035] The present step is a step for forming an anode 101 on a glass substrate 102. In preferred practice, glass substrate 102 will be one that resists attack by chemicals such as acids, alkalis, etc., and that is mass-producible. An ITO transparent electrode was formed to a thickness of 0.1  $\mu\text{m}$  on substrate 102 and patterned at 100  $\mu\text{m}$  pitch.

Partitioning member formation step (Fig. 1B)

[0036] The present step is a step for forming a partitioning member 103 on glass substrate 102. Specifically, non-photosensitive polyimide (partitioning member) buried between anodes (ITO electrodes) and also serving as an ink drip prevention wall (bank) was formed by photolithography. The non-photosensitive polyimide was 20  $\mu\text{m}$  wide and 2.0  $\mu\text{m}$  thick.

Composition for a hole injecting and transporting layer discharge step (Fig. 1C)

[0037] Hole injecting and transporting layer Compositions 1 through 3 (106 in the drawing) were discharged from the head 105 of an ink-jet printing device (Epson MJ-800C) 104 to effect patterning. film formation of a hole injecting and transporting layer 107. After patterning film formation, a hole injecting and transporting layer was formed through a drying treatment (200°C, 10 min). During discharge of the composition for a hole injecting and transporting layer, no bank-overflowing application was observed, and a high-precision hole injecting and transporting layer pattern was achieved.

Light-emitting layer composition filling step (Fig. 1D)

[0038] Next, a PPV precursor (poly(para-phenylene vinylene)) composition was manufactured as a green light-emitting layer. A light-emitting layer composition 108 was discharged by an ink-jet system to effect patterning film formation of a light-emitting layer 109. Rhodamine B-doped PPV, which exhibits red light emission, or coumarin-doped PPV, which exhibits blue light emission, could be used for the light-emitting layer 109 as well. Light-emitting layers exhibiting light emission of the three primary colors (red, green, blue) can be subjected to patterning over a hole injecting and transporting layer to produce a highly detailed full-color organic EL display.

Cathode formation step (Fig. 1E)

[0039] Finally, a cathode 100 was deposited so as to cover the light-emitting layer 109, forming an organic EL element.

(Hole injecting and transporting layer film formation evaluation)

[0040] In the organic EL element manufacturing steps described above, the number of discharges of the composition for a hole injecting and transporting layer was varied, and the hole injecting and transporting layer film thickness and sheet resistance were measured, as well as evaluating film formation. Results are given in Table 13.

Table 13

| Composition | Discharge no. | Film thickness [ $\mu\text{m}$ ] | Resistance [ $\Omega/\text{m}^2\text{a}$ ] | Film-forming properties | Luminance [ $\text{cd}/\text{m}^2\text{a}$ ] |
|-------------|---------------|----------------------------------|--|-------------------------|--|
| 1           | 1             | 0.05                             | $5.0 \times 10^9\text{a}$                  | O                       | 2000   |
|             | 3             | 0.14                             | $1.7 \times 10^9\text{a}$                  | O                       | 1900   |
|             | 5             | 0.26                             | $0.9 \times 10^9\text{a}$                  | X                       | 1600   |
| 2           | 1             | 0.03                             | $0.7 \times 10^9\text{a}$                  | Display Problem         | 2000   |
|             | 3             | 0.1                              | $0.2 \times 10^9\text{a}$                  | X                       | 1500   |
|             | 5             | 0.14                             | $0.1 \times 10^9\text{a}$                  | X                       | 1500   |
| 3           | 1             | 0.02                             | $0.5 \times 10^9\text{a}$                  | Display Problem         | 2000   |
|             | 3             | 0.06                             | $0.2 \times 10^9\text{a}$                  | O                       | 1800   |
|             | 5             | 0.1                              | $0.1 \times 10^9\text{a}$                  | X                       | 1400   |

[0041] From these results, it will be apparent that in the case of a low-molecular weight material, where the hole injecting and transporting layer film thickness is 0.05  $\mu\text{m}$  or smaller and film resistance is from  $0.5 \times 10^9 \Omega/\text{m}^2$  to  $5 \times 10^9 \Omega/\text{m}^2$ , light-emission characteristics are good.

(Effect)

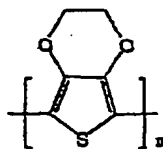
[0042] According to the present aspect of the embodiment, fine patterning can be realized easily, in a short time, and at low cost. Accordingly, there is no risk of leakage due to the hole injecting and transporting layer itself, a problem that could not be solved in solid film formation methods. Further, since film thickness can be readily controlled through manipulation of the discharge amount or number of discharges, optimization of thin film design thereby is possible.

Aspect of Embodiment of the Invention 2.

[0043] The present aspect of embodiment is one in which the conductive compound for forming the hole injecting and transporting layer is a material capable of forming a film from solution (high-molecular weight material), and is one that employs polyaniline, polysilane, or other conductive high-molecular weight material. In particular, as water can be used as the principal solvent, and as characteristics can be adjusted through the mixture ratio, a mixed material of PEDT (polyethylene dioxythiophene)

Chemical Formula 1

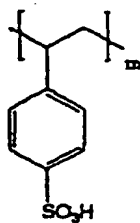
[0044]



and PSS (polystyrene sulfonic acid)

Chemical Formula 2

[0045]



is preferred.

(Example)

[0046] Compositions for a hole injecting and transporting layer prepared using a PEDT/PSS mixture aqueous solution as the high-molecular weight material (hole injecting and transporting layer component) were prepared in the five varieties (Composition 11 through Composition 15) given in Table 14 through Table 18.

Table 14

| Composition 11                                  |  |               |
|---|--|---------------|
| Composition                                     | Material name                                | Content (wt%) |
| Hole injecting and transporting layer component | PEDT/PSS mixture aqueous dispersion(1.0 wt%) | 20            |
| Polar solvent                                   | water  | 80            |

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| Composition 11 |               |               |
|----------------|---------------|---------------|
| Composition    | Material name | Content (wt%) |
| Lubricant      | --            | 0             |

Table 15

| Composition 12                                  |  |               |
|---|--|---------------|
| Composition                                     | Material name                                | Content (wt%) |
| Hole injecting and transporting layer component | PEDT/PSS mixture aqueous dispersion(1.0 wt%) | 20            |
| Polar solvent                                   | N,N-dimethyl formamide                       | 75            |
| Lubricant                                       | glycerin                                     | 5             |

Table 16

| Composition 13                                  |  |               |
|---|--|---------------|
| Composition                                     | Material name                                | Content (wt%) |
| Hole injecting and transporting layer component | PEDT/PSS mixture aqueous dispersion(1.0 wt%) | 20            |
| Polar solvent                                   | water  | 75            |
| Lubricant                                       | glycerin                                     | 55            |

Table 17

| Composition 14                                  |  |               |
|---|--|---------------|
| Composition                                     | Material name                                | Content (wt%) |
| Hole injecting and transporting layer component | PEDT/PSS mixture aqueous dispersion(1.0 wt%) | 20            |
| Polar solvent                                   | water  | 70            |
|   | methanol                                     | 5             |
| Lubricant                                       | glycerin                                     | 5             |

Table 18

| Composition 15                                  |  |               |
|---|--|---------------|
| Composition                                     | Material name                                | Content (wt%) |
| Hole injecting and transporting layer component | PEDT/PSS mixture aqueous dispersion(1.0 wt%) | 20            |
| Polar solvent                                   | water  | 65            |
|   | ethoxy ethanol                               | 10            |
| Lubricant                                       | glycerin                                     | 5             |

[0047] Discharge evaluations were conducted using an ink-jet printing device (Epson MJ-800C). Film-forming properties evaluations were conducted in film state after a heating treatment (200°C, 10-60 min) conducted after application through discharge. Viscosity [is expressed as] measured values at 20°C.

Table 19

| Composition | Contact angle[°] | Viscosity [cps] | Surface tension [dyne/cm] | Discharge properties | Film-forming properties |
|-------------|------------------|-----------------|---------------------------|----------------------|-------------------------|
| 1           | 130              | 1.2             | 73.0                      | X                    | -                       |

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| Composition | Contact angle[°] | Viscosity [cps] | Surface tension [dyne/cm] | Discharge properties | Film-forming properties |
|-------------|------------------|-----------------|---------------------------|----------------------|-------------------------|
| 2           | 63               | 0.9             | 38.5                      | X                    | -                       |
| 3           | 120              | 4.5             | 68.0                      | O                    | )                       |
| 4           | 84               | 4.0             | 62.3                      | Display Problem«     | O                       |
| 5           | 64               | 3.5             | 40.0                      | Display Problem«     | Display Problem«        |

[0048] From the preceding results, it will be apparent that the concentration of the conductive high-molecular weight material is preferably 0.01 wt%-10.0 wt% based on the entire composition, and especially preferably 0.1 wt%-5.0 wt%. The reason is that if the conductive high-molecular weight material concentration is too low, a large number of discharges will be needed to produce the required film thickness, and mass-production efficiency will be poor, while on the other hand, if the conductive high-molecular weight material concentration is too high, viscosity will be higher.

[0049] In preferred practice, the composition for a hole injecting and transporting layer will contain a lubricant. This can effectively prevent drying and solidification of the ink composition in the ink-jet nozzle mouth. Examples of the lubricant are glycerin, diethylene glycol, and other polyhydric alcohols; glycerin is especially preferred. In preferred practice, the added amount of lubricant is equivalent to about 5 wt%-20 wt% based on the entire composition.

[0050] In preferred practice, water, a mixed solvent of water and a lower alcohol, or a mixed solvent of water and a Cellosolve solvent will be used as the polar solvent used for the composition for a hole injecting and transporting layer. The use of these solvents makes it possible to adjust the contact angle of the composition for a hole injecting and transporting layer with respect to the material of the nozzle face of the ink-jet head, the viscosity, and the surface tension without any loss of solubility or dispersibility of the conductive compound. Methanol or ethanol is preferred as the lower alcohol. From the standpoint of film-forming properties, ethoxy ethanol is preferred as the Cellosolve solvent.

[0051] Other additives, as well as film stabilizing materials, may be added as well; for example, viscosity modifiers, antioxidants, pH modifiers, preservatives, resin emulsions, leveling agents, etc., may be used.

(Manufacturing process for composition for a hole injecting and transporting layer)

[0052] A comparison of film-forming properties and light emission characteristics with and without sonication and a filtration step was conducted using the composition for a hole injecting and transporting layer (Composition 15) given in Table 18, and is given in Table 7. PPV (poly(para-phenylene vinylene)) was used as a green light-emitting layer.

Table 20

| step                                |     | Film quality     | luminance [cd/m <sup>2</sup> ·a] | light emission initial voltage[V <sup>th</sup> ·a] | light emission lifetime [hr] |
|-------------------------------------|-----|------------------|----------------------------------|--|------------------------------|
| sonication step and filtration step | yes | Display Problem« | 2000                             | 3.0  | 5000                         |
|                                     | no  | )                | 1000                             | 5.0  | 500                          |

[0053] As will be apparent from the preceding results, conducting sonication increases the dispersion, and the use of a composition prepared by filtration of a sonicated dispersion affords a homogeneous hole injecting and transporting layer that has good flatness. In preferred practice, film thickness is 0.05 µm-0.1 µm. The reason is that the film-forming properties of the hole injecting and transporting layer affect the light emission characteristics of the element.

[0054] The manufacturing steps for the organic EL element of the present aspect of embodiment are the same as in Aspect of Embodiment 1.

INDUSTRIAL APPLICABILITY

[0055] According to the present invention, a composition for a hole injecting and transporting layer is prepared as a liquid, thus permitting optimal design of materials, and the liquid composition is prepared as an ink, thus permitting high-precision patterning of a hole injecting and transporting layer by ink-jet system. Further, the use

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of a conductive compound, particularly a high-molecular weight material, as the hole injecting and transporting layer material affords manufacture of an organic EL element having high reliability and high qualities.

[0056] According to the ink-jet system patterning which pertains to the present invention, there is provided simple, low-cost hole injecting and transporting layer formation.

[0057] According to the manufacturing process for an organic EL element which pertains to the present invention, film thickness, number of dots, and other parameters can be adjusted in a desired manner, allowing the size and pattern of a light-emitting element to be established in a desired manner as well. Further, by combining light-emitting layers of the three primary colors (red, green, blue) produced through ink-jet system patterning, it is possible to develop a highly detailed full-color display with excellent light emission characteristics.

## Claims

1. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of 30° to 170°.

2. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the viscosity is within the range of 1 cps to 20 cps.

3. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the surface tension is within the range of 20 dyne/cm to 70 dyne/cm.

4. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of 30° to 170°, and the viscosity is within the range of 1 cps to 20 cps.

5. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the viscosity is within the range of 1 cps to 20 cps, and the surface tension is within the range of 20 dyne/cm to 70 dyne/cm.

6. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the surface tension is within the range of 20 dyne/cm to 70 dyne/cm, and the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of 30° to 170°.

7. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of 30° to 170°, the viscosity is within the range of 1 cps to 20 cps, and the surface tension is within the range of 20 dyne/cm to 70 dyne/cm.

8. The composition for a hole injecting and transporting layer according to any of Claims 1 through 7, wherein the conductive compound is either a high-molecular weight material or a low-molecular weight material.

9. The composition for a hole injecting and transporting layer according to any of Claims 1 through 8, wherein the concentration of the conductive compound is in the range of 0.01 wt% to 10 wt%.

10. The composition for a hole injecting and transporting layer according to any of Claims 1 through 9, wherein the conductive compound is present in a dissolved or dispersed state in a polar solvent as the solvent.

11. The composition for a hole injecting and transporting layer according to Claim 10, wherein the polar solvent is a mixed solvent of water and a lower alcohol.

12. The composition for a hole injecting and transporting layer according to Claim 11, wherein the lower alcohol is methanol or ethanol.

13. The composition for a hole injecting and transporting layer according to Claim 10, wherein the polar solvent is a mixed solvent of water and a Cellosolve solvent.

14. The composition for a hole injecting and transporting layer according to Claim 13, wherein the Cellosolve solvent is ethoxy ethanol.

15. The composition for a hole injecting and transporting layer according to any of Claims 1 through 14, wherein the composition comprises a lubricant.

16. The composition for a hole injecting and transporting layer according to Claim 15, wherein the lubricant is glycerin.

17. A manufacturing process for the composition for a hole injecting and transporting layer according to any of Claims 1 through 16, comprising:

a sonication step; and

a filtration step.

18. A manufacturing process for an organic EL element having a stacked structure of a hole injecting and transporting layer and a light-emitting layer formed within a partitioning member divided into individual pixel areas, comprising:

a step wherein a partitioning member provided with openings corresponding to pixel areas is formed on a substrate;

a step wherein an ink-jet type recording head is used to fill the aforementioned openings with the composition for a hole injecting and transporting layer according to any of Claims 1 through 17; and

a step wherein the composition for a hole injecting and transporting layer that has filled the openings is subjected to a drying process to form a hole injecting and transporting layer.

19. An organic EL element manufactured by the manufacturing process according to Claim 18.

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20. An organic EL element manufactured by the manufacturing process according to Claim 18, wherein the film thickness of the hole injecting and transporting layer is 0.1  $\mu\text{m}$  or less.

21. An organic EL element manufactured by the manufacturing process according to Claim 18, wherein the film resistance of the hole injecting and transporting layer is in the range  $0.5 \times 10^9 \Omega/\text{m}^2$  to  $5 \times 10^9 \Omega/\text{m}^2$ .

Amended claims under Art. 19.1 PCT

1. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of  $30^\circ$  to  $170^\circ$ , and the content of the conductive compound is in the range of 0.01 wt% to 10 wt%.

2. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the viscosity is within the range of 1 cps to 20 cps, and the content of the conductive compound is in the range of 0.01 wt% to 10 wt%.

3. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the surface tension is within the range of 20 dyne/cm to 70 dyne/cm, and the content of the conductive compound is in the range of 0.01 wt% to 10 wt%.

4. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of  $30^\circ$  to  $170^\circ$ , the viscosity is within the range of 1 cps to 20 cps, and the content of the conductive compound is in the range of 0.01 wt% to 10 wt%.

5. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the viscosity is within the range of 1 cps to 20 cps, the surface tension is within the range of 20 dyne/cm to 70 dyne/cm, and the content of the conductive compound is in the range of 0.01 wt% to 10 wt%.

6. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the surface tension is within the range of 20 dyne/cm to 70 dyne/cm, the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of 30° to 170°, and the content of the conductive compound is in the range of 0.01 wt% to 10 wt%.

7. A composition for a hole injecting and transporting layer for use in patterning formation of a hole injecting and transporting layer of an organic EL element using an ink-jet type recording head, comprising:

a conductive compound; and

a solvent;

wherein the viscosity is within the range of 1 cps to 20 cps, the surface tension is within the range of 20 dyne/cm to 70 dyne/cm, the contact angle with respect to the material making up the ink discharge nozzle face of the ink-jet type recording head is within the range of 30° to 170°, and the content of the conductive compound is in the range of 0.01 wt% to 10 wt%.

8. The composition for a hole injecting and transporting layer according to any of Claims 1 through 7, wherein the conductive compound is either a high-molecular weight material or a low-molecular weight material.

9. The composition for a hole injecting and transporting layer according to any of Claims 1 through 8, wherein the conductive compound is present in a dissolved or dispersed state in the solvent as a polar solvent.

10. The composition for a hole injecting and transporting layer according to Claim 9, wherein the polar solvent is a mixed solvent of water and a lower alcohol.

11. The composition for a hole injecting and transporting layer according to Claim 10, wherein the lower alcohol is methanol or ethanol.

12. The composition for a hole injecting and transporting layer according to Claim 9, wherein the polar solvent is a mixed solvent of water and a Cellosolve solvent.

13. The composition for a hole injecting and transporting layer according to Claim 12, wherein the Cellosolve solvent is ethoxy ethanol.

14. The composition for a hole injecting and transporting layer according to any of Claims 1 through 13, further comprising a lubricant.

15. The composition for a hole injecting and transporting layer according to Claim 14, wherein the lubricant is glycerin.

16. A manufacturing process for the composition for a hole injecting and transporting layer according to any of Claims 1 through 15, comprising:

a sonication step; and

a filtration step.

17. A manufacturing process for an organic EL element having a stacked structure of a hole injecting and transporting layer and a light-emitting layer formed within a partitioning member divided into individual pixel areas, comprising:

a step wherein a partitioning member provided with openings corresponding to pixel areas is formed on a substrate;

a step wherein an ink-jet type recording head is used to fill the aforementioned openings with the composition for a hole injecting and transporting layer according to any of Claims 1 through 16; and

a step wherein the composition for a hole injecting and transporting layer that has filled the openings is subjected to a drying process to form a hole injecting and transporting layer.



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18. An organic EL element manufactured by the manufacturing process according to Claim 17.

19. An organic EL element manufactured by the manufacturing process according to Claim 17, wherein the film thickness of the hole injecting and transporting layer is 0.1  $\mu\text{m}$  or less.

20. An organic EL element manufactured by the manufacturing process according to Claim 17, wherein the film resistance of the hole injecting and transporting layer is in the range  $0.5 \times 10^9 \Omega/\text{m}^2$  to  $5 \times 10^9 \Omega/\text{m}^2$ .

Fig.1A

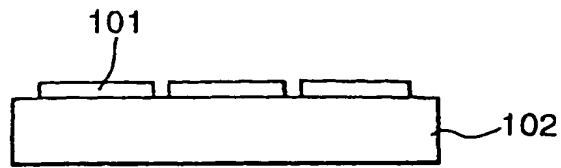


Fig.1B

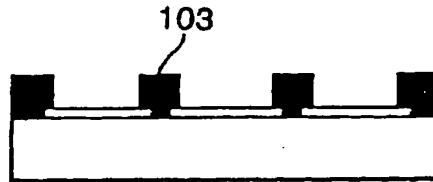


Fig.1C

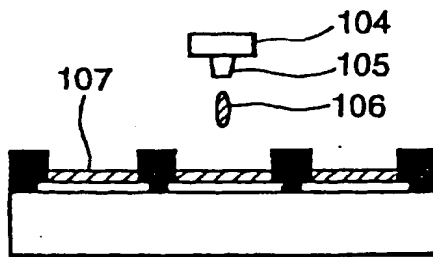


Fig.1D

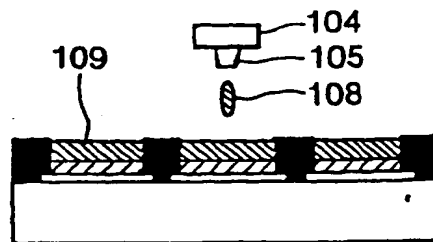
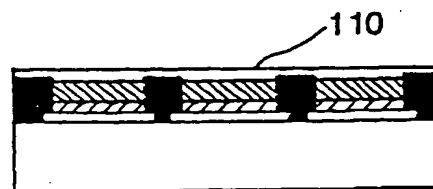


Fig.1E



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP98/03935

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>Int.Cl. <sup>6</sup> H05B33/10, 33/22, C08L101/00, C08K5/05<br>According to International Patent Classification (IPC) or to both national classification and IPC  |  |  |
|---|--|--|
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>Int.Cl. <sup>6</sup> H05B33/10, 33/22, C08L101/00, C08K5/05, C09D11/00<br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>Jitsuyo Shinan Koho 1940-1996 Toroku Jitsuyo Shinan Koho 1994-1998<br>Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998<br>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) |  |  |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>   |  |  |
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.  |
| Y   | JP, 7-235378, A (Casio Computer Co., Ltd.),<br>5 September, 1995 (05. 09. 95),<br>Full text ; Figs. 1 to 10 (Family: none) | 1-21   |
| PY  | JP, 10-153967, A (Seiko Epson Corp.),<br>9 June, 1998 (09. 06. 98),<br>Full text ; Figs. 1 to 6 (Family: none)             | 1-21   |
| PY  | JP, 10-12377, A (Seiko Epson Corp.),<br>19 June, 1996 (19. 06. 96),<br>Full text ; Figs. 1 to 3 (Family: none)             | 1-21   |
| Y   | JP, 6-136306, A (Canon Inc.),<br>17 May, 1994 (17. 05. 94),<br>Full text (Family: none)                                    | 1-8  |
| A   | JP, 1-204977, A (Fuji Rubber Co., Ltd.),<br>17 August, 1989 (17. 08. 89),<br>Full text (Family: none)                      | 1-21   |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.  |  |  |
| * Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed           |  | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br>"A" document member of the same patent family |
| Date of the actual completion of the international search<br>2 December, 1998 (02. 12. 98)  |  | Date of mailing of the international search report<br>15 December, 1998 (15. 12. 98)   |
| Name and mailing address of the ISA/<br>Japanese Patent Office  |  | Authorized officer   |
| Facsimile No.   |  | Telephone No.  |

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International application No.  
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| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |   |                       |
|---|---|-----------------------|
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages              | Relevant to claim No. |
| A   | JP, 4-170478, A (Seiko Epson Corp.),<br>18 June, 1992 (18. 06. 92),<br>Full text (Family: none) | 1-21                  |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)